Rovibrational Spectroscopic Constants and Fundamental Vibrational Frequencies for Isotopologues of Cyclic and Bent Singlet HC$_2$N isomers

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ABSTRACT

Through established, highly-accurate *ab initio* quartic force fields (QFFs), a complete set of fundamental vibrational frequencies, rotational constants, and rovibrational coupling and centrifugal distortion constants have been determined for both the cyclic $1\,^1A'$ and bent $2\,^1A'$ DCCN, $H^{13}CCN$, $HC^{13}CN$, and $HCC^{15}N$ isotopologues of HCCN. Spectroscopic constants are computed for all isotopologues using second-order vibrational perturbation theory (VPT2), and the fundamental vibrational frequencies are computed with VPT2 and vibrational configuration interaction (VCI) theory. Agreement between VPT2 and VCI results is quite good with the fundamental vibrational frequencies of the bent isomer isotopologues in accord to within a 0.1 to 3.2 cm^{-1} range. Similar accuracies are present for the cyclic isomer isotopologues. The data generated here serve as a reference for astronomical observations of these closed-shell, highly-dipolar molecules using new, high-resolution telescopes and as reference for laboratory studies where isotopic labeling may lead to elucidation of the formation mechanism for the known interstellar molecule: $X\,^3A'$ HCCN.

Keywords: astrochemistry $-$ (stars:) circumstellar matter $-$ ISM: lines and bands $-$ ISM: molecules $-$ molecular data $-$ radio lines: ISM

1. Introduction

A better understanding of cyanomethylene, HC_2N, in its various triplet and singlet, bent and cyclic isomers is necessary in order to fully explore the carbon-nitrogen chemistry of astrochemical environments. The ground state, bent-triplet radical form of cyanomethylene, HC_2N, is believed to be a key intermediate in the formation of various nitriles, such as

cyanogen (C_2N_2) or dicyanogen (C_4N_2), in Titan's atmosphere (Yung 1987). Additionally, this radical has been detected in the interstellar medium (ISM) towards the carbon-rich star IRC+10 216 (Guélin & Cernicharo 1991), but interstellar formation pathways have not yet been able to explain the existence of this molecule in any molecular clouds (Fukuzawa et al. 1998). Even so, molecules of related size, geometrical arrangement, and number of electrons have also been detected in the ISM. These include l/c-C_3H (Thaddeus et al. 1985a; Yamamoto et al. 1987), c/l-C_3H_2 (Thaddeus et al. 1985b; Cernicharo et al. 1991), and potentially $1\ ^1A'$ C_3H^- in its quasilinear form (Fortenberry et al. 2013b). Hence, the interstellar existence of the various isomers and spin multiplicities of HC_2N is likely.

It has been recently shown via highly-accurate quantum chemical computations that the bent-triplet HC_2N isomer, known to exist in the ISM, is the lowest energy form of cyanomethylene (Inostroza et al. 2011). However, a local minimum pertaining to the cyclic-singlet form is known to be stable, as well (Mebel & Kaiser 2002). It is 7.8 kcal mol^{-1} higher in energy than the bent-triplet according to these same highly-accurate computations (Inostroza et al. 2011). A bent-singlet isomer lies at 11.1 kcal mol^{-1} higher in energy than the ground state (Inostroza et al. 2011). The stability of $1\ ^1A'$ c-HC_2N over the bent-singlet isomer is due to its aromaticity. As such, it is isoelectronic with cyclopropenylidene (c-C_3H_2) the smallest aromatic molecule detected in the ISM (Thaddeus et al. 1985b); C_3H^-, a new anion believed to be present in the Horsehead nebula photodissociation region (Fortenberry et al. 2013b); and c-$C_3H_3^+$, an aromatic cation likely to exist in the ISM, as well, (Huang et al. 2011). The deuterated istopologues of c-$C_3H_3^+$ are necessary for interstellar detection through rotational spectroscopy (Huang & Lee 2011) unless vibrational detection proves fruitful. Since $1\ ^1A'$ c-HC_2N contains one less atom and three fewer degrees-of-freedom, its interstellar detection would make it the smallest interstellar aromatic molecule, at least by those criteria.

The CH_2CN radical has been detected in the ISM by Irvine et al. (1988), and its presence could also lead to the creation of cyanomethylene. Protonation of CH_2CN followed by dissociative electron recombination would result in HCCN and H_2. Since this reaction is similar to the proposed mechanism for the interstellar creation of cyclopropenylidene (Lee et al. 1985, 2009; Huang et al. 2011; Huang & Lee 2011), the singlet aromatic isomer may be formed preferentially over the bent-triplet. It has also been speculated that CH_2CN^- may be present in the ISM (Fortenberry et al. 2013a), and simple proton attachment could also yield HCCN and H_2. Such a reaction could lead to creation of the bent-singlet isomer which, through intersystem crossing or internal rearrangement, could lead to the triplet form or cyclize to create the aromatic isomer. The reaction of $C(^3P_j)$ + HCN has also been probed as a possible pathway leading to the creation of HC_2N (Mebel & Kaiser 2002), but details of the various stages of such a mechanism have not been fully explored. Simple photolysis of a C−H bond in CH_2CN may also lead to either of the bent isomers. However, one of the most promising formation pathways for the cyclic isomer is an exact analog for the formation of cyclopropenylidene – that is, through deprotonation of the most stable form of $C_2H_2^+$, since it has been shown that the most stable isomer has a cyclic structure similar to cyclopropenylidene (Kokkila et al. 2013).

In order to understand the mechanisms that lead to the creation of any potential interstellar isomer of HC_2N, laboratory astrophysical simulations would benefit greatly from highly-accurate reference data, especially for the isotopologues. Isotopic labeling can be used to elucidate the reaction pathway for specific atoms within the reactive species. New astronomical observatories, such as the Atacama Large Millimeter Array (ALMA) and the Stratospheric Observatory for Infrared Astronomy (SOFIA), have exceptional spectral resolution. As a result, isotopically substituted forms of various interstellar molecules can be readily resolved from their standard forms. Rovibrational reference data computed from highly-accurate quartic force fields has been provided for various molecular systems

of astronomical significance encompassing the aforementioned cyclopropenylidene (Lee et al. 1985, 2009) and c-$C_3H_3^+$ (Huang et al. 2011; Huang & Lee 2011) as well as $HOCO^+$ (Fortenberry et al. 2012), l-C_3H^+ and quasilinear C_3H^- of significance to the Horsehead nebula (Huang et al. 2013b; Fortenberry et al. 2013b), $NNOH^+$ (Huang et al. 2013a) and many other molecular species including the bent-triplet, cyclic-singlet, and bent-singlet forms of HC_2N (Inostroza et al. 2011). In this paper, we are extending the understanding of the rovibrational nature of the HC_2N systems by providing the spectroscopic constants and fundamental vibrational frequencies for the singly-substituted DCCN, $H^{13}CCN$, $HC^{13}CN$, and $HCC^{15}N$ isotopologues of cyclic $1\,^1A'$ and bent $2\,^1A'$ HCCN.

2. Computational Details

The reference geometries for the isotopologues of both HC_2N isomers are taken from the main isotopologues computed in Inostroza et al. (2011). The quartic force fields (QFFs) computed therein provide the necessary potential surface to carry out the rovibrational computations of the isotopologues due to use of the Born-Oppenheimer approximation in the formulation of the QFFs. The 3-pt (tz,qz,5z)+core+rel QFF is the most accurate of those utilized previously (Inostroza et al. 2011) and will be employed here. Recently, we have shortened the nomenclature for this QFF to the CcCR QFF (Fortenberry et al. 2011a,b).

Spectroscopic constants and vibrational fundamental frequencies have been determined from second order perturbation theory (Mills 1972; Papousek & Aliev 1982; Watson 1977) with the SPECTRO program (Gaw et al. 1991). Second-order vibrational perturbation theory (VPT2) is capable of predicting fundamental vibrational frequencies to within a few cm^{-1} (Martin & Taylor 1997; Huang & Lee 2008) when the QFF is accurate enough and effects of any Fermi resonances are included properly (Martin et al. 1995). Vibrational

fundamental frequencies are also determined from vibrational configuration interaction (VCI) theory using the MULTIMODE program (Carter et al. 1998; Bowman et al. 2003) after the force constants are transformed into the Morse-cosine coordinate system which gives proper limiting behavior (Dateo et al. 1994; Fortenberry et al. 2013c). The complete Watson S-reduced asymmetric top Hamiltonian is adopted allowing for direct quantitative comparison between the theoretical spectroscopic constants and those from experiment which has been analyzed using this Hamiltonian.

3.   Discussion

3.1.   Isotopologues of bent-singlet HC$_2$N

The ground-state vibrationally averaged rotational constants and fundamental vibrational frequencies obtained for the bent 2 $^1A'$ DCCN, H^{13}CCN, HC^{13}CN, and HCC^{15}N isotopologues are given in Table 1. Harmonic frequencies and anharmonic constants are presented in Table 2. Constants which are affected by any Fermi and/or Coriolis resonance are indicated in this table. Vibration-rotation interaction constants as well as the quartic and sextic centrifugal distortion constants are presented in Table 3. All of these isotopologues possess C_s symmetry, and their dipole-moments are 3.06 D neglecting vibrational averaging. The Born-Oppenheimer equilibirum geometries of these isotopologues are identical to those for the main isotopologue reported in Inostroza et al. (2011). The VCI computations are computed at the four-mode representation (4MR) level with 21 primitive harmonic oscillator basis functions contracted down to 11 basis functions with 16 Hermite-Gauss (HEG) quatrature points for $\nu_2 - \nu_5$. The ν_6 mode is described by 31 primitives, 21 contracted functions, and 21 HEG points with ν_1 described by 21 primitives, 9 contracted functions, and 16 HEG points.

The rotational constants differ for each of the isotopologues compared to one another and the main isotopologue of $2\ ^1A'$ bent-singlet HCCN. The variance in the rotational constants is great enough for each to be distinguished in laboratory astrophysical experiments or high-resolution astronomical observations. Even though B_0 and C_0 for $HC^{13}CN$ are nearly exactly the same values (11 099 MHz and 10 862 MHz) as they are for HCCN, the 542 421 MHz $HC^{13}CN$ A_0 differs enough from the HCCN 543 130 MHz A_0 such that the rotational energy levels should be distinguishable with the use of modern instruments.

The greatest isotopic shift in the fundamental vibrational frequencies for the bent-singlet isotopologues is the ν_1 C$-$D stretch in DCCN. VPT2 and VCI report this frequency to be slightly larger than 2187 cm^{-1}, a decrease of over 700 cm^{-1} from the ν_1 C$-$H stretch in HCCN. This shift also brings the C-D stretch within range of the EXES instrument on the Stratospheric Observatory for Infrared Astronomy (SOFIA). The ν_1 hydrogen stretching modes for the other istopologues are also well-behaved in that both VPT2 and VCI report similar frequencies for each system analyzed. The CcCR QFF for other closed-shell tetra-atomic systems has produced hydrogen stretching frequencies that are known to be within 1 cm^{-1} or better of experiment (Fortenberry et al. 2012; Huang et al. 2013a) indicating that these frequencies reported here should provide highly accurate reference data. Additionally, the good agreement for the two vibrational methods for each of the other modes of these isotopologues indicates that the frequencies reported are accurate. Even the torsional frequencies are no more than 2.2 cm^{-1} different (for $H^{13}CCN$), whereas previous studies have shown that VCI often experiences difficulty with describing this mode (Fortenberry et al. 2011a,b; Mladenović 2012). Such is not the case here.

The ν_2 mode of $HC^{13}CN$ is represented equally by two different states and subsequent frequencies for both VPT2 and VCI. That is, the ν_2, $\nu_3 + \nu_4$, and $2\nu_3$ states are more

strongly coupled in a resonance polyad for this isotopologue than for the others, and hence there will be intensity sharing with the combination and overtone bands. The two frequencies (eigenvalues) which exhibit the largest ν_2 character are listed in Table 1. Given the degree of mixing, it is likely that both bands would be observable and thus we report both here.

3.2. Isotopologues of cyclic-singlet HC_2N

Isomeric cyclization to the aromatic cyclic-singlet form of HC_2N greatly changes the rotational constants compared to the quasilinear, bent-singlet isomer. A_0, B_0, and C_0 are listed in Table 4 and are all of the same order of magnitude. The difference between the A_0 and B_0-type constants is each greater than about 10 000 MHz for each of the isotopologues listed here. A_0 is 40 744 MHz, and B_0 is 34 505 MHz for the main isotopologue (Inostroza et al. 2011): a difference of only about 6 000 MHz (Inostroza et al. 2011). Due to the cyclization, the rotational spectra of the isotopologues of the cyclic-singlet HC_2N will vary noticeably.

The harmonic vibrational frequencies and associated anharmonic constants are given in Table 5 with those constants affected by Fermi and/or Coriolis resonances marked, once more. Finally, the vibration-rotation interaction constants as well as the Watson S-reduced Hamiltonian constants are listed in Table 6. The same basis 4MR VCI computations are employed for the cyclic-singlet isotopologues as are for the linear isomers described previously except that ν_1 is now utilizing 11 contracted vibrational basis functions. These isotopologues also all posses C_s symmetry, and their CCSD(T)/cc-pVQZ dipole-moments are 1.7 D as with the main isotopologue of cyclic 1 $^1A'$ HCCN (Inostroza et al. 2011) neglecting vibrational averaging.

The VPT2 and VCI methods once again produce fundamental vibrational frequencies that are in close agreement with one another. There is a bit more deviation with the cyclic isomer isotopologues between the two methods than there was with the bent singlet. As shown in Table 4, the largest difference is for the ν_5 fundamental. These differ between VPT2 and VCI by 7.5 cm^{-1} for each of the heavy atom isotopologues but only by 3.9 cm^{-1} for the deuterated form. Similar behavior is present in the main isotopologue where the difference between VPT2 and VCI is also 7.5 cm^{-1} (Inostroza et al. 2011). Since this mode involves a bending motion terminating with the hydrogen atom, the decrease in frequency and in VPT2/VCI difference is expected upon deuteration. Hence, the modes behave as expected for each of the isotopologues even when the two methods are not coincident.

As is typical for the various ways in which to implement single-isotopic substitution, deuteration changes the frequencies greatest and decreases their values for each mode. The other isotopologues are affected by their substitutions as compared to one another and the main isotopologue, but the effect on the vibrational frequencies is significantly reduced. The H^{13}CCN and HCC^{15}N isotopologues have quite closely related rotational constants, but their fundamental vibrational frequencies are far enough apart for astronomical distinction to be possible. For instance, the ν_1 C$-$H stretches are more than 10 cm^{-1} different at 3123.3 cm^{-1} and 3135.7 cm^{-1}, respectively, for VCI. HC^{13}CN and HCC^{15}N share fundamental vibrational frequencies that are often within 4 cm^{-1} of each other. However, the ν_2 and ν_3 modes have frequencies that differ by 15 cm^{-1}, as computed by VCI, allowing for these isotopologues to be conclusively differentiated whether in the ISM or in the laboratory.

4. Conclusions

Even though the only isotopically substituted systems known to date in the ISM consist mainly of deuterium-laden small molecules (Turner & Zuckerman 1978), more

resolving power brought to bear on the ISM and various other astronomical environments will be able to distinguish spectral features in the vibrational and rotational portions of the electromagnetic spectrum brought about by various isotopologues. Deuterium is four times more abundant than ^{13}C in the ISM, but this isotope of carbon is actually more plentiful as a nucleus than the most common nuclear arrangements of argon, calcium, and sodium (Savage & Sembach 1996). Hence, ^{13}C reference data is necessary for spectral analyses of the ISM.

Furthermore, a more full understanding of interstellar chemical synthesis and reaction mechanisms in which the isomers of HC_2N should be of significance may require experiments that employ isotopic labeling as part of the schema. This technique is highly beneficial with regards to rotational and vibrational spectroscopy where atoms can be labeled as having been produced from certain reactants. More information regarding the nature of the spectroscopic shifts brought about by isotopic substitution provides important information which will benefit ISM simulations in the laboratory, especially since the mechanism for the interstellar synthesis of the detected $X\ ^3A'$ HCCN radical has not yet been established. The fundamental vibrational frequencies, rotational constants, and other spectroscopic constants given as a part of this study should provide clear data points for determining how chemical pathways in the ISM or in circumstellar shells may lead to the creation of this family of molecules.

5.   Acknowledgements

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Table 1: CcCR Rotational constants (MHz), and Fundamental Vibrational Frequencies (cm^{-1}) for the Bent, Singlet HC_2N Isomer Isotopologues.

	DCCN		$H^{13}CCN$		$HC^{13}CN$		$HCC^{15}N$	
A_0	307 257		537 301		542 421		543 095	
B_0	10 366		10 695		11 099		10 755	
C_0	10 010		10 473		10 862		10 533	
	VPT2[a]	VCI	VPT2[b]	VCI	VPT2[c]	VCI	VPT2[b]	VCI
$\nu_1\ (a')$	2187.4	2187.2	2925.5	2925.4	2936.1	2932.9	2933.2	2933.5
$\nu_2\ (a')$	2042.3	2041.0	2043.3	2042.4	2016.0^d	2015.5^d	2031.5	2029.6
					1948.0^d	1950.5^d		
$\nu_3\ (a')$	1001.6	1001.3	1035.9	1034.6	1043.1	1042.8	1039.6	1039.3
$\nu_4\ (a')$	797.1	797.7	939.6	938.7	952.8	950.4	956.8	954.1
$\nu_5\ (a')$	311.5	309.7	323.8	320.6	316.8	313.9	323.3	320.2
$\nu_6\ (a'')$	401.7	401.1	444.4	442.4	436.1	434.3	443.0	441.1

[a]The $\nu_2 = 2\nu_3$, $\nu_4 = 2\nu_6$, and $\nu_6 = 2\nu_5$ Fermi resonances are included.
[b]$\nu_1 = \nu_2 + \nu_4$, $\nu_2 = 2\nu_3 = 2\nu_4 = \nu_4 + \nu_3$, $\nu_3 = 2\nu_6$, and $\nu_4 = 2\nu_6$ Fermi resonance polyads.
[c]Require the $\nu_1 = \nu_2 + \nu_4$, $\nu_4 = 2\nu_6$, and $\nu_2 = 2\nu_3 = 2\nu_4 = \nu_4 + \nu_3$ Fermi resonance polyads.
[d]These states are coupled at 50%-50% from the $\nu_2 = \nu_4 + \nu_3$ and $\nu_2 = 2\nu_3$ bases.

Table 2: Harmonic Frequencies (ω in cm^{-1}) and Anharmonic Constants (χ_{ij} in cm^{-1}) from VPT2 for the Bent, Singlet HC$_2$N Isotopologues.[a]

	mode	1	2	3	4	5	6
DCCN	ω	2259.8	2061.4	1010.5	808.7	290.4	397.0
	1	-35.131					
	2	0.131	-14.562				
	3	-0.144	3.084*	-7.533*			
	4	-0.496	-9.552	-0.346	-6.676		
	5	-0.675	-4.817	8.573	20.864	0.098*	
	6	-2.901	-2.932	0.989	-1.635*	17.892*	-0.321*
H^{13}CCN	ω	3063.7	2067.3	1050.1	955.1	293.6	429.0
	1	-65.804					
	2	2.643*	-14.502				
	3	-14.524	-5.211*	-2.494*			
	4	4.451*	-5.290*	-18.120*	-7.053*		
	5	-1.357	-4.789	15.139	15.771	-0.417	
	6	-3.574	-3.220	-3.200*	0.443*	37.419	0.731*
HC^{13}CN	ω	3072.7	2019.2	1057.7	969.9	286.8	420.4
	1	-66.243					
	2	2.587*	-13.927				
	3	-14.805	-3.042*	-2.557*			
	4	4.756*	-6.930*	-14.900*	-8.989*		
	5	-1.300	-4.411	12.216	16.272	-0.166	
	6	-3.491	-2.971	1.595	1.134*	37.966	-0.670*
HCC^{15}N	ω	3072.8	2041.9	1053.7	972.4	292.8	427.6
	1	-66.238					
	2	2.463*	-13.897				
	3	-14.521	-4.650*	-2.348*			
	4	4.821*	-6.243*	-16.518*	-8.262*		
	5	-1.317	-4.927	14.356	16.704	-0.375	
	6	-3.599	-3.301	-3.705*	0.752*	37.694	0.784*

[a]Constants marked with an asterisk (*) are effected by Fermi resonances.

Table 3: The Vibration-Rotation Interaction Constants with the Quartic and Sextic Centrifugal Distortion Constants for the Bent, Singlet HC$_2$N Isotopologues.

	mode	α^A	$10^3\ \alpha^B$	$10^3\ \alpha^C$		(MHz)		(Hz)		(MHz)		(Hz)
		Vib-Rot Constants (cm^{-1})			Distortion Constants				Watson S Reduction			
DCCN	1	0.3953	0.3254	0.6799	τ'_{aaaa}	-402.220	$10^{-6}\ \Phi_{aaa}$	0.1308	$10^3\ D_J$	4.3754	$10^3\ H_J$	-0.2210
	2	-0.0729	1.9329	1.7168	τ'_{bbbb}	-0.019	$10^3\ \Phi_{bbb}$	1.8036	D_{JK}	0.4736	$10^{-6}\ H_K$	0.1314
	3	0.0820	1.8333	1.6876	τ'_{cccc}	-0.016	$10^3\ \Phi_{ccc}$	-0.3344	D_K	100.0770	H_{JK}	1.8650
	4	-0.7255	0.3360	0.3658	τ'_{aabb}	-2.001	$10^{-4}\ \Phi_{aab}$	0.0914	$10^3\ d_1$	-0.1907	$10^{-4}\ H_{KJ}$	-0.0268
	5	0.3623	-1.5686	-2.2946	τ'_{aacc}	-0.073	Φ_{abb}	3.3315	$10^3\ d_2$	-0.0471	$10^3\ h_1$	0.4251
	6	-0.1540	-1.5137	-0.4531	τ'_{bbcc}	-0.018	$10^{-4}\ \Phi_{aac}$	-0.1480			$10^3\ h_2$	0.4778
							$10^3\ \Phi_{bbc}$	-0.8421			$10^3\ h_3$	0.1094
							Φ_{acc}	-0.4080				
							$10^3\ \Phi_{bcc}$	0.0929				
							Φ_{abc}	3.5721				
H^{13}CCN	1	0.8694	0.4815	0.7634	τ'_{aaaa}	-904.812	$10^{-6}\ \Phi_{aaa}$	0.4743	$10^3\ D_J$	4.7678	$10^3\ H_J$	-1.9183
	2	-0.0824	1.8911	1.7687	τ'_{bbbb}	-0.020	$10^3\ \Phi_{bbb}$	-1.5017	D_{JK}	0.9067	$10^{-6}\ H_K$	0.4761
	3	-0.4553	0.1742	0.2030	τ'_{cccc}	-0.019	$10^3\ \Phi_{ccc}$	-1.8083	D_K	225.2914	H_{JK}	2.1856
	4	-0.8877	1.0754	1.6178	τ'_{aabb}	-3.132	$10^{-4}\ \Phi_{aab}$	0.1199	$10^3\ d_1$	-0.0773	$10^{-4}\ H_{KJ}$	-0.1744
	5	0.4588	-1.5759	2.4348	τ'_{aacc}	-0.533	Φ_{abb}	3.8937	$10^3\ d_2$	-0.0188	$10^3\ h_1$	0.0499
	6	-0.0849	-1.3196	-0.4044	τ'_{bbcc}	-0.019	$10^{-4}\ \Phi_{aac}$	-0.2940			$10^3\ h_2$	0.1316
							$10^3\ \Phi_{bbc}$	-2.7712			$10^3\ h_3$	0.0267
							Φ_{acc}	-0.9949				
							$10^3\ \Phi_{bcc}$	-2.4068				
							Φ_{abc}	3.3797				
HC^{13}CN	1	0.8823	0.4906	0.7932	τ'_{aaaa}	-929.216	$10^{-6}\ \Phi_{aaa}$	0.4958	$10^3\ D_J$	5.0614	$10^3\ H_J$	-1.9945
	2	-0.0832	1.8959	1.7673	τ'_{bbbb}	-0.021	$10^3\ \Phi_{bbb}$	1.4717	D_{JK}	0.9425	$10^{-6}\ H_K$	0.4980
	3	-0.2796	0.5122	0.4383	τ'_{cccc}	-0.020	$10^3\ \Phi_{ccc}$	-1.8746	D_K	231.3564	H_{JK}	2.4878
	4	-1.0715	0.8384	1.5280	τ'_{aabb}	-3.302	$10^{-4}\ \Phi_{aab}$	0.1120	$10^3\ d_1$	-0.0871	$10^{-4}\ H_{KJ}$	-0.2249
	5	0.4490	-1.5252	-2.4775	τ'_{aacc}	-0.508	Φ_{abb}	4.4152	$10^3\ d_2$	-0.0214	$10^3\ h_1$	0.0678
	6	-0.0774	-1.3668	-0.3732	τ'_{bbcc}	-0.020	$10^{-4}\ \Phi_{aac}$	-0.3365			$10^3\ h_2$	0.1606
							$10^3\ \Phi_{bbc}$	-2.8791			$10^3\ h_3$	0.0329
							Φ_{acc}	-1.1210				
							$10^3\ \Phi_{bcc}$	-2.4315				
							Φ_{abc}	3.8860				
HCC^{15}N	1	0.8855	0.4701	0.7551	τ'_{aaaa}	-933.539	$10^{-6}\ \Phi_{aaa}$	0.5060	$10^3\ D_J$	4.7120	$10^3\ H_J$	-1.6918
	2	-0.0810	1.9762	1.8501	τ'_{bbbb}	-0.020	$10^3\ \Phi_{bbb}$	-1.2402	D_{JK}	0.8957	$10^{-6}\ H_K$	0.5080
	3	-0.3624	0.3385	0.2804	τ'_{cccc}	-0.018	$10^3\ \Phi_{ccc}$	-1.5971	D_K	232.4843	H_{JK}	2.2676
	4	-1.0061	0.9423	1.5747	τ'_{aabb}	-3.134	$10^{-4}\ \Phi_{aab}$	0.1117	$10^3\ d_1$	-0.0784	$10^{-4}\ H_{KJ}$	-0.2060
	5	0.4729	-1.5901	-2.4607	τ'_{aacc}	-0.486	Φ_{abb}	3.9910	$10^3\ d_2$	-0.0189	$10^3\ h_1$	0.0618
	6	-0.0908	-1.3513	-0.4222	τ'_{bbcc}	-0.019	$10^{-4}\ \Phi_{aac}$	-0.3174			$10^3\ h_2$	0.1366
							$10^3\ \Phi_{bbc}$	-2.4361			$10^3\ h_3$	0.0275
							Φ_{acc}	-0.9979				
							$10^3\ \Phi_{bcc}$	-2.0766				
							Φ_{abc}	3.5154				

Table 4: CcCR Rotational constants (MHz), and Fundamental Vibrational Frequencies (cm^{-1}) for the Cyclic, Singlet HC$_2$N Isomer Isotopologues.

	DCCN		H^{13}CCN		HC^{13}CN		HCC^{15}N	
A_0	42 505		43 549		41 784		43 783	
B_0	27 137		31 172		31 934		30 843	
C_0	16 508		18 106		18 038		18 034	
	VPT2^a	VCI	VPT2^b	VCI	VPT2^b	VCI	VPT2^b	VCI
ν_1 (a')	2364.2	2364.8	3125.4	3123.3	3146.6	3139.7	3137.9	3135.7
ν_2 (a')	1530.7	1535.8	1548.0	1551.3	1565.0	1569.4	1552.8	1556.3
ν_3 (a')	1270.3	1271.0	1272.9	1273.5	1274.4	1274.9	1288.6	1289.2
ν_4 (a')	961.9	965.6	1011.3	1010.3	1003.1	1002.2	1004.6	1003.6
ν_5 (a')	665.7	669.6	821.9	829.5	817.5	825.0	820.3	827.8
ν_6 (a'')	712.3	715.5	888.2	893.4	895.2	900.6	895.8	901.1

^{a}Fermi resonance $\nu_1 = 2\nu_3$, $\nu_2 = 2\nu_6$, and $\nu_3 = 2\nu_6$.
^{b}Fermi resonance $\nu_1 = 2\nu_2$ and $\nu_2 = 2\nu_5$.

Table 5: VPT2 Harmonic Frequencies (ω in cm^{-1}) and Anharmonic Constants (χ_{ij} in cm^{-1}) for the Cyclic, Singlet HC$_2$N Isotopologues.[a]

	mode	1	2	3	4	5	6
DCCN	ω	2447.8	1566.2	1300.0	982.8	682.4	722.7
	1	-30.440					
	2	-7.134*	-6.019				
	3	-0.927*	-10.332	-7.764*			
	4	-3.816*	-11.877*	-3.770*	-5.684		
	5	-10.343	-4.852*	-9.837	-0.483	-2.349*	
	6	-12.024*	-4.195*	-3.091	-0.848*	1.465	-0.954
H^{13}CCN	ω	3256.0	1585.9	1303.8	1033.0	846.2	903.8
	1	59.532					
	2	0.163*	-6.399*				
	3	5.202	-13.226	-8.658			
	4	-7.988	-11.013	-4.734	-5.882		
	5	-11.738	-7.780	-12.348	0.436	-4.347	
	6	-18.661	-3.880*	-2.179	3.435	0.188	-2.491*
HC^{13}CN	ω	3268.4	1605.9	1305.8	1024.5	841.8	911.1
	1	-59.828					
	2	0.130*	-7.158*				
	3	5.418	-12.631	-9.242			
	4	-8.000	-10.464	-4.437	-5.767		
	6	-11.725	-8.043	-12.147	0.135	-4.185	
	5	-18.905	-4.253*	-1.875	3.193	0.010	-2.481*
HCC^{15}N	ω	3268.4	1591.8	1320.7	1025.9	844.7	911.7
	1	-59.821					
	2	-0.457*	-6.321*				
	3	6.161	-14.137	-9.287			
	4	-8.094	-10.381	-4.584	-5.750		
	6	-11.798	-7.817	-12.281	0.003	-4.240	
	5	-18.902	-4.138*	-2.190	3.375	-0.013	-2.486*

[a]Constants marked with an asterisk (*) are effected by Fermi resonances.

Table 6: The Vibration-Rotation Interaction Constants with the Quartic and Sextic Centrifugal Distortion Constants for the Bent, Cyclic HC$_2$N Isotopologues.

	mode	Vib-Rot Constants (cm^{-1}) $10^3\ \alpha^A$	$10^3\ \alpha^B$	$10^3\ \alpha^C$	Distortion Constants	(MHz)		(Hz)	Watson S Reduction	(MHz)		(Hz)
DCCN	1	1.0151	6.7105	2.3987	τ'_{aaaa}	-1.046	Φ_{aaa}	1.2976	$10^3\ D_J$	29.4974	H_J	-0.0889
	2	4.8758	2.9533	1.7461	τ'_{bbbb}	-0.287	Φ_{bbb}	0.1845	D_{JK}	0.0943	H_K	0.1002
	3	-7.3478	6.5594	0.0946	τ'_{cccc}	-0.037	$10^3\ \Phi_{ccc}$	0.9380	D_K	0.1378	H_{JK}	0.7138
	4	13.6639	-5.5447	4.5789	τ'_{aabb}	-0.439	Φ_{aab}	-1.3223	$10^3\ d_1$	-15.6296	H_{KJ}	0.5725
	5	7.8960	-0.3740	1.3038	τ'_{aacc}	-0.102	Φ_{abb}	0.9510	$10^3\ d_2$	-5.5381	h_1	0.0113
	6	4.7235	0.7867	-1.0642	τ'_{bbcc}	-0.057	Φ_{aac}	-1.3693			h_2	0.0908
							Φ_{bbc}	-0.3484			h_3	0.0346
							$10^3\ \Phi_{acc}$	3.2513				
							$10^3\ \Phi_{bcc}$	2.9068				
							Φ_{abc}	-0.7194				
H^{13}CCN	1	1.3758	5.3985	1.8673	τ'_{aaaa}	-0.957	Φ_{aaa}	2.2695	$10^3\ D_J$	47.0510	H_J	-0.2262
	2	5.8996	3.5017	2.0028	τ'_{bbbb}	-0.447	Φ_{bbb}	0.2123	D_{JK}	0.1284	H_K	11.9200
	3	-9.7725	7.7552	-0.1389	τ'_{cccc}	-0.048	$10^3\ \Phi_{ccc}$	-1.6691	D_K	0.0640	H_{JK}	4.4589
	4	10.3389	-7.0449	4.8384	τ'_{aabb}	-0.447	Φ_{aab}	-2.6891	$10^3\ d_1$	-25.0151	H_{KJ}	-13.8830
	5	-5.2204	2.4058	0.2573	τ'_{aacc}	-0.118	Φ_{abb}	2.3314	$10^3\ d_2$	-7.4304	h_1	0.0577
	6	6.0343	2.9535	-0.0663	τ'_{bbcc}	-0.078	Φ_{aac}	-2.6121			h_2	0.1661
							Φ_{bbc}	-0.4394			h_3	-0.0046
							Φ_{acc}	-0.3634				
							Φ_{bcc}	0.2515				
							Φ_{abc}	1.7327				
HC^{13}CN	1	1.6802	5.4319	1.9440	τ'_{aaaa}	-0.816	Φ_{aaa}	3.1321	$10^3\ D_J$	40.7400	H_J	-0.1896
	2	7.6012	1.7533	1.7570	τ'_{bbbb}	-0.437	Φ_{bbb}	0.1996	D_{JK}	0.1388	H_K	16.2296
	3	-8.9013	6.4131	0.3045	τ'_{cccc}	-0.048	$10^3\ \Phi_{ccc}$	-1.3777	D_K	0.0245	H_{JK}	4.9027
	4	9.0429	-6.9980	4.5697	τ'_{aabb}	-0.612	Φ_{aab}	-4.3067	$10^3\ d_1$	-24.3109	H_{KJ}	-17.8106
	5	-6.2665	4.9733	0.2444	τ'_{aacc}	-0.105	Φ_{abb}	2.5085	$10^3\ d_2$	-9.9308	h_1	0.0646
	6	5.5075	3.0396	-0.6841	τ'_{bbcc}	-0.088	Φ_{aac}	-3.8452			h_2	0.1443
							Φ_{bbc}	-0.4047			h_3	-0.0143
							Φ_{acc}	-0.6337				
							Φ_{bcc}	0.4281				
							Φ_{abc}	4.3390				
HCC^{15}N	1	1.3751	5.9187	1.9400	τ'_{aaaa}	-0.861	Φ_{aaa}	2.8485	$10^3\ D_J$	46.9030	H_J	-0.2345
	2	5.7200	3.4593	1.9216	τ'_{bbbb}	-0.472	Φ_{bbb}	0.1826	D_{JK}	0.0870	H_K	18.1082
	3	-9.2015	7.5726	0.1418	τ'_{cccc}	-0.048	$10^3\ \Phi_{ccc}$	-1.1259	D_K	0.0814	H_{JK}	6.2878
	4	9.7118	-7.5702	4.6694	τ'_{aabb}	-0.497	Φ_{aab}	-4.2982	$10^3\ d_1$	-26.5077	H_{KJ}	-21.3130
	5	-5.3496	2.9436	2.4289	τ'_{aacc}	-0.120	Φ_{abb}	3.0016	$10^3\ d_2$	-9.0646	h_1	0.0993
	6	5.6539	3.3988	-0.6961	τ'_{bbcc}	-0.077	Φ_{aac}	-5.4312			h_2	0.1626
							Φ_{bbc}	-0.4890			h_3	-0.0533
							Φ_{acc}	-1.0599				
							Φ_{bcc}	0.8296				
							Φ_{abc}	9.3652				